

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平6-80709

(43) 公開日 平成6年(1994)3月22日

(51) Int.Cl. ⁵	識別記号	庁内整理番号	F I	技術表示箇所
C 0 8 F 2/20	MBK	7442-4 J		
B 0 1 F 17/52				
C 0 8 F 2/22	MBL	7442-4 J		
216/06	MKV	6904-4 J		
C 0 9 C 3/10	PBX	6904-4 J		

審査請求 未請求 請求項の枚数(全 7 頁)

(21) 出願番号 特願平3-282170

(22) 出願日 平成3年(1991)10月2日

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(54) 【発明の名称】 分散剤

(57) 【要約】

【目的】 ビニル化合物の乳化重合用分散剤として用いると、生成皮膜の耐水性に優れかつ粘度の温度依存性が小さい重合体エマルジョンを与えることができ、また、ビニル化合物の懸濁重合用分散剤として用いると、均一な多孔性粒子からなり可塑剤吸収速度が大きく、残留モノマーの除去が容易な重合体を生成することができる分散剤を提供する。また、顔料その他の被分散物質に高い分散力を示し、比較的低粘度で高濃度の分散液を生成する分散剤を提供する。

【構成】 炭素数4以下の α -オレフィン単位を1~10モル%含有する変性ポリビニルアルコール分散剤。特に、ビニル化合物の乳化重合用および懸濁重合用分散剤、ならびに顔料の分散剤。

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【特許請求の範囲】

【請求項1】 炭素数4以下の α -オレフィン単位を1～10モル%含有する変性ポリビニルアルコールからなる分散剤。

【請求項2】 請求項1記載の変性ポリビニルアルコールからなるビニル化合物の乳化重合用分散剤。

【請求項3】 請求項1記載の変性ポリビニルアルコールからなるビニル化合物の懸濁重合用分散剤。

【請求項4】 請求項1記載の変性ポリビニルアルコールからなる顔料用分散剤。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、変性ポリビニルアルコールからなる分散剤、特にビニル化合物の乳化重合および懸濁重合用分散剤ならびに顔料分散用分散剤に関する。

【0002】

【従来技術とその問題点】ポリビニルアルコール（以下、「PVA」と略す）はビニル化合物、特に酢酸ビニルに代表されるビニルエステル類の乳化重合用分散剤として広く用いられており、これを用いて乳化重合して得られるビニルエステル重合体エマルジョンは各種接着剤、塗料、紙または繊維加工などの分野で用いられている。

【0003】ところがビニルエステル重合体エマルジョンは、接着性や作業性は優れるが、皮膜の耐水性に劣り、またエマルジョン粘度の温度依存性が大きいという欠点を有しており、これらの性質は乳化重合に用いた分散剤に依るところが大であることが知られている。

【0004】すなわち、乳化重合用分散剤としてのPVAには、一般的にはけん化度98モル%程度のいわゆる“完全けん化PVA”とけん化度88モル%程度の“部分けん化PVA”があり、前者を使用した場合、比較的水性には良好なものの、低温時のエマルジョン粘度の上昇が著しく、ゲル化し易いという欠点がある。他方、後者のPVAを使用した場合、エマルジョンの低温時の粘度上昇やゲル化傾向は改善されるものの皮膜の耐水性が劣るという欠点を有している。

【0005】このような欠点を改良するために、両者のPVAの併用、両者の中間的なけん化度のPVAの使用が行なわれているが皮膜の耐水性とエマルジョン粘度の小さな温度依存性の両者を十分満足するに至っていない。また、皮膜の耐水性を向上させるために乳化剤として部分けん化PVAを用いて得た重合体エマルジョンに尿素樹脂や各種架橋剤を添加することも行なわれている。これらの方法によって、ある程度耐水性は改良されるものの、粘度上昇などにより使用時の作業性が低下し、充分満足すべき結果は得られていない。

【0006】また、塩化ビニルその他のビニル化合物の懸濁重合においては、従来、部分けん化PVAおよびメ

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チルセルロース、カルボキシメチルセルロースなどのセルロース誘導体が分散剤として用いられてきた。

【0007】ビニル化合物の懸濁重合において、分散剤は、得られる重合体の品質を支配する重要な因子であって、一般に、分散剤に要求される性能としては、(I)少量の使用で高い分散力を示し、得られる重合体粒子の粒径分布をできるだけシャープにする働きのあること、

(II)可塑剤の吸収速度を大きくして加工性を容易にするため、および重合体粒子中に残存するビニルモノマーの除去を容易にするため、さらに成形品にフィッシュアイまでの生成を防止するため、重合体粒子をできるだけ均一にしかも多孔性にする働きがあること、(III)充てん比重の大きい重合体粒子をつくる働きがあることなどが挙げられる。

【0008】しかしながら、従来用いられてきた上述の懸濁重合用分散剤は、これらの要求性能を満足するものではなく、重合体粒子を多孔性にする能力が低く、重合体の可塑剤吸収速度を大きくすることがなく、残留ビニルモノマーの除去が困難であるという欠点があった。また、一般に、分散剤としては高度の分散力を有し、比較的低粘度で高濃度の分散液を生成することが要求されている。

【0009】

【発明が解決しようとする課題】本発明の目的は、従来の乳化重合用および懸濁重合用PVA分散剤の欠点を解消し、ビニル化合物の乳化重合に用いるとき、生成皮膜の耐水性に優れかつ粘度の温度依存性が小さい重合体エマルジョンを与えることができ、また、ビニル化合物の懸濁重合に用いるとき、均一な多孔性粒子からなり、可塑剤吸収速度が大きく、残留モノマーの除去が容易な重合体を生成することができる分散剤を提供するにある。

【0010】本発明の他の目的は、顔料その他の被分散物質に対し高い分散力を有し、比較的低粘度で高濃度の分散液を生成することができる分散剤を提供するにある。

【0011】

【課題を解決するための手段】上記の目的は、本発明の分散剤、すなわち、炭素数4以下の α -オレフィン単位を1～10モル%含有する変性ポリビニルアルコールからなる分散剤によって達成される。

【0012】本発明において用いられる炭素数4以下の α -オレフィン単位を1～10モル%含有する変性PVAは、ビニルエステルと炭素数4以下の α -オレフィンとの共重合体をけん化することによって得られる。ビニルエステルとしては、塩酸ビニル、酢酸ビニル、プロピオン酸ビニルなどが挙げられるが、酢酸ビニルが経済的にみて好ましい。

【0013】ビニルエステルと共重合される α -オレフィンには炭素数4以下のもので、例えばエチレン、プロピレン、n-ブテン、イソブチレンなどが挙げられるが、

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得られる重合体皮膜の耐水強度の点でエチレンが好ましい。変性PVA中の α -オレフィンの含有量は1~10モル%、好ましくは2~8モル%である。 α -オレフィンの含有量が1モル%未満の場合には、上述の顕著な効果が得られず、逆に10モル%を超える場合には、水溶性が低下し、やはり上述の効果が得られない。

【0014】なお、本発明の変性PVAには、本発明の趣旨を損なわない範囲で他の官能基、例えば、カルボキシル基、ラクトン基、アミド基、アミノ基などが導入されていてもよい。本発明の変性PVAのけん化度は50モル%~99モル%の範囲であることが好ましい。また、重合度は100~8,000の範囲で適宜選ばれる。

【0015】本発明の変性PVAの代表的な用途は、ビニル化合物の乳化重合用および懸濁重合用分散剤である。ビニル化合物の乳化重合および懸濁重合の代表例としては、酢酸ビニルに代表されるビニルエステルの乳化ホモ重合および酢酸ビニルとエチレン、プロピレン、塩化ビニル、アクリル酸エステル類、メタクリル酸エステル類との乳化共重合；ならびに塩化ビニル、スチレン、メタクリル酸メチルその他のメタクリル酸エステルなどの懸濁重合が挙げられる。

【0016】本発明の変性PVAを乳化重合用分散剤として用いる場合、ビニル化合物に対して0.1~20重量%、好ましくは0.3~15重量%が使用される。使用量が0.1重量%未満では重合安定性に乏しく、20重量%を超えると得られるエマルジョンの耐水性が低下する。本発明の変性PVA乳化重合用分散剤は単独使用が望ましいが、本発明の目的を損なわない範囲で、他の保護コロイドや乳化剤の使用も可能である。例えば、従来のPVA、でんぶん、ポリアクリルアミド、ヒドロキシエチルセルロース、従来公知のノニオン性乳化剤、アニオン性乳化剤などが併用できる。

【0017】本発明の変性PVA分散剤を懸濁重合用分散剤として用いる場合、従来のPVA分散剤と同様に用いることができる。さらに、本発明の変性PVA分散剤は、無機顔料および有機顔料を始めとし、多くの被分散物質に対し高い分散力を示すので、多くの分野で従来の分散剤に代え用いることができる。特に、顔料の分散剤として用いると、従来の多くの分散剤と比較して、低粘度で分散安定性のよい分散液を生成する。

【0018】

【発明の効果】本発明の変性PVA分散剤は、ビニル化合物の乳化重合用分散剤として用いると、生成皮膜の耐水性に優れかつ粘度の温度依存性が小さい重合体エマルジョンを得ることができる。また、ビニル化合物の懸濁重合に用いると、粒径分布がシャープでかつ多孔性があり、しかも充填比の大きい懸濁重合体粒子が得られる。この懸濁重合体は可塑性の吸収速度が大きく、残存モノマーの除去が容易であり、取扱い時の粉の飛散が少

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なく、また、成型機へのくい込み性がよいという特性も持っている。

【0019】さらに、本発明の変性PVA分散剤は、被分散物質に対し高い分散力を示す。特に、顔料の分散剤として用いると、従来の多くの分散剤と比較して、低粘度で分散安定性のよい分散液を生成することができる。

【0020】

【実施例】以下、実施例について本発明の変性PVA分散剤を具体的に説明する。各実施例において「部」は重量基準である。

実施例1

(変性PVAの製造) 攪拌機を備えた反応容器に酢酸ビニル100部とメタノール30部を仕込み、次いで、空素置換した後エチレン3部を在入した。開始剤として2,2'-アゾビスイソブチロニトリルをメタノールに溶解した溶液を調製し、空素ガスによるバブリングによって空素置換した。上記のモノマーを仕込んだ反応容器を昇温し、内温が60℃に達したとき開始剤溶液を注入し、重合を開始した。3時間後に重合率が48%に達したところで冷却した。脱エチレンし、次いで、減圧下に未反応酢酸ビニルモノマーを除去し、メタノール溶液とし、これにNaOHメタノール溶液を添加し、けん化した。得られた変性PVAは重合度1,200、けん化度90.0モル%、エチエン含有量7.2モル%であった。

【0021】(酢酸ビニルの乳化重合) 攪拌機、還流冷却器、温度計、滴下ロートを備えた反応器中で前記PVA20gを水240gに溶解した。次ぎに、酢酸ビニル20gを添加し、内温が70℃に達したところで過酸化水素0.3gおよび酒石酸0.5gを添加し、重合を開始した。続いて、酢酸ビニル180gと過酸化水素0.3gを3時間かけて連続的に添加した。添加終了後、内温を80℃に1時間保持し熟成を行なった。冷却後ジブチルフタレート20gを添加し、不揮発分48.0%、30℃での粘度12,000cPのエマルジョンを得た。

【0022】得られたエマルジョンを以下の試験に供した。

(1) エマルジョン粘度の温度依存性評価

30℃および0℃でエマルジョン粘度を測定し、その粘度比(0℃/30℃)で温度依存性を評価した。

(2) 低温放置安定性

-5℃で24Hr放置し、エマルジョンの変化の有無を観察した。

(3) 耐水性

次の条件により紙/紙の接着試験を行ない、1日養生乾燥後30℃の水中に24時間浸漬後剥離し、その接着状態を調べ、3段階(A:非常に良好、B:良好、C:不良)で評価した。

紙 : Bライナー、25mm×50mm大、各5片

塗布量: 40g (wet) / m²

圧 縮: ハンドローラーにて1回圧縮

養生: 23℃、65%RH、24hr

結果を表1に示す。

【0023】実施例2, 3

(変性PVAの製造) 単量体組成を変えた他は実施例1と同様の操作で2種の変性PVAを製造した。

(酢酸ビニルの乳化重合) 上記PVAをそれぞれ分散剤として用い、実施例1と同様に操作して酢酸ビニルの乳化重合を行い、得られたエマルジョンを評価した。結果*10

*を表1に示す。

【0024】比較例1, 2

(PVAの製造) 単量体組成を変えた他は実施例1と同様の操作で未変性PVAを得た。

(酢酸ビニルの乳化重合) 上記未変性PVAをそれぞれ分散剤として用い、実施例1と同様に操作して酢酸ビニルの乳化重合を行い、得られたエマルジョンを評価した。結果を表1に示す。

【0025】

【表1】

酢酸ビニルの重合処方および重合体エマルジョンの特性

例	PVA分散剤				重合体エマルジョン特性		
	けん化度 *1 (モル%)	エチレン 含量 (モル%)	重合度	固形分 濃度 (重量%)	生成直後の 粘度 (30℃) (mPas・S)	0℃での 粘度 (mPas・S)	0℃粘度 /30℃ 粘度比
実施例1	90.0	7.2	1,200	48.0	12,000	30,000	2.5
実施例2	85.0	10.0	500	47.9	9,000	24,300	2.7
実施例3	94.0	4.0	1,700	47.8	28,000	72,800	2.6
比較例1	98.0	0	1,700	48.1	15,800	192,800	12.2
比較例2	88.0	0	1,700	48.4	41,000	114,800	2.8

*1 ビニルアルコール含量

表1の結果から、本発明の変性PVA分散剤を用いると、耐水性のよい皮膜を生成することができ、かつ、エマルジョン粘度の温度依存性が小さいエマルジョンが得られることが明白である。

【0026】実施例4～6および比較例3

(塩化ビニルの懸濁重合) 単量体組成を変えた他は前記実施例1とほぼ同様な操作を繰返して、変性PVAおよび未変性PVAを製造した。これらを単独ないしは他の

PVAとともに分散剤として用いて塩化ビニルの懸濁重合を下記方法で実施した。

【0027】ガラスライニングオートクレーブに脱イオン水40部、PVA系分散剤の2重量%水溶液0.75部およびジイソプロピルパーオキシジカーボネートの50重量%トルエン溶液0.009部を仕込み、オートクレーブ内を50mmHgとなるまで脱気して酸素を除いた後、塩化ビニルモノマーを30部仕込み、攪拌下に57℃に昇温して重合を行なった。重合開始時、オートクレーブ内の圧力は8.5kg/cm²Gであったが、重合開始7時間後に4.5kg/cm²Gとなったので、この時点で重合を停止し、未反応塩化ビニルモノマーをバージし、内容物を取り出し脱水乾燥した。PVA系分散剤の物性と使用量を表2に、得られた塩化ビニル樹脂の特性を表3に示す。塩化ビニル樹脂の重合収率は85%で、平均重合度は1050であった。

【0028】得られた塩化ビニル樹脂の特性は下記の基準により評価した。

(1) 粒径分布：タイラメッシュ基準の金網を使用して乾式篩分析により測定した。

(2) 充てん比重：JIS K6721-1959によって測定した。

【0029】(3) 粒子多孔性の均一性：塩化ビニル樹

脂100部、ジオクチルフタレート50部、ジブチル錫マレエート1部、セチルアルコール1部、チタン白0.25部、カーボンブラック0.1部からなる混合物を150℃のロールで所定時間(3分、5分、7分)混練し、肉厚0.2mmのシートを作成し、これに光を透過させて100cm²当りのシート中に含まれるフィッシュ・アイの数を数えた。フィッシュ・アイが短時間のうちになくなるものほど粒子多孔性の均一性がよいことを示している。

10 【0030】(4) 可塑剤吸収性：プラストグラフに接続させたプラネタリーミキサーを用い、80℃に保った容器内に塩化ビニル樹脂100部、ジオクチルフタレート50部を投入し、攪拌しながら各時間毎の混練トルクを記録し、混練トルクが低下した点における混練時間を表示した。時間が短いほど可塑剤の吸収性がよいことを示している。

(5) 残留塩化ビニルモノマー：塩化ビニル樹脂の一定量をテトラヒドロフランに溶解してガスクロマトグラフにより塩化ビニル樹脂中の塩化ビニルモノマー含有量を

20 定量した。

【0031】

【表2】

塩化ビニルの重合処方

例	PVA分散剤				併用PVA分散剤		
	けん化度 *1 (モル%)	重合度	エチレン含量 (モル%)	使用量 *2 (重量%/VCM)	けん化度 *1 (モル%)	重合度	使用量*2 (重量%/VCM)
実施例4	75	700	5.0	0.06	—	—	—
実施例5	80	1,800	10.0	0.06	—	—	—
実施例6	30	200	8.0	0.04	80	200	0.04
比較例3	80	2,000	0	0.08	—	—	—

*1 ビニルアルコール含量

*2 塩化ビニルモノマー(VCM)に対する重量%

【0032】

【表3】

塩化ビニル樹脂の特性

例	粒径分布 (重量%)			高比重 (g/cc)	粒子多孔性の均一性 (フィッシュテイルの個数)			可塑剤 吸収性 (分)	残存 塩化ビニル モノマー (ppm)
	42 μ 以上	100 μ 以上	250 μ 以上		3分	5分	7分		
実施例 4	100	56	0	0.551	40	1	0	5.3	0.7
実施例 5	100	50	0	0.550	39	2	0	5.1	0.6
実施例 6	100	53	0	0.530	35	0	0	4.2	0.1
比較例 3	100	38	0	0.492	700	50	13	15.0	120

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表3の結果から、本発明の変性PVA分散剤を単独または従来公知のPVAと併用して懸濁重合を行うと、均一な多孔性粒子からなり、可塑剤吸収速度が大きく、残留モノマーの除去が容易なビニル重合体を得られることが判る。

【0033】実施例6、7および比較例4、5

(炭酸カルシウム分散液の調製) 前記の実施例に準じた方法で変性PVAおよび未変性PVAを調製し、これらを分散剤として用いて炭酸カルシウム(白石工業製P-3)の濃度60重量%のペーストを得た。このペーストを20℃にて3ヶ月放置し、その分散状態を3段階法(A:分散状態に変化なし、B:わずかに沈降を生じた、C:かなり沈降を生じた)で評価した。なお、比較のために、ポリアクリル酸ソーダを分散剤として用いてペーストを調製し、同様に評価した。結果を表4に示す。

【0034】

【表4】

20

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例	P V A 分 散 剤				炭酸カルシウム分散液	
	けん化度 *1 (モル%)	重合度	エチレン含量 (モル%)	使用量 (重量%/炭カル)	粘度 (30°C) (mPas・S)	放置安定性
実施例6	85	200	5.0	1.0	150	A
実施例7	88	300	10.0	1.0	200	A
比較例4	38	300	0	1.0	1,500	C
比較例5	ポリアクリル酸ソーダ			1.0	850	B

*1 ビニルアルコール含量

表4の結果から、本発明の変性PVA分散剤は低粘度で分散安定性のよい分散液を与えることが判る。

(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Publication Number of Patent Application: JP-A-6-80709

(43) Date of Publication of Application: March 22, 1994

(51) Int.Cl. ⁵		Id. No.	Intraof. Ref. No.	FI
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C08F	2/20	MBK	7442-4J	
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B01F	17/52		7619-4F	
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C08F	2/22	MBL	7442-4J	
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	216/06	MKV	6904-4J	
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C09C	3/10	PBX	6904/4J	
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Request for Examination: not made

Number of Claims: 4 (7 pages in total)

(21) Application Number: Hei 3-282170

(22) Application Date: October 2, 1991

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(54) [Title of the Invention] DISPERSANT

(57) [Abstract]

[Object] To provide a dispersant capable, when employed as a dispersant for emulsion polymerization of a vinyl compound, of providing a polymer emulsion showing an excellent water resistance in a generated film and a low temperature dependence of viscosity, and, when employed as a dispersant for suspension polymerization of a vinyl compound, of generating a polymer constituted of uniform porous particles showing a high plasticizer absorbing speed and enabling an easy removal of a remaining monomer. Also to provide a dispersant showing a high dispersing power to a dispersed substance such as a pigment or the like, and capable of generating a dispersion liquid of a relatively low viscosity and a high concentration.

[Structure] A dispersant comprising modified polyvinyl alcohol containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol.%. In particular, a dispersant for emulsion polymerization and suspension polymerization of a vinyl compound, and a dispersant for a pigment.

[Claims]

[Claim 1] A dispersant comprising modified polyvinyl alcohol containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol. %.

[Claim 2] A dispersant for emulsion polymerization of a vinyl compound, comprising modified polyvinyl alcohol according to claim 1.

[Claim 3] A dispersant for suspension polymerization of a vinyl compound, comprising modified polyvinyl alcohol according to claim 1.

[Claim 4] A dispersant for a pigment, comprising modified polyvinyl alcohol according to claim 1.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application]

The present invention relates to a dispersant comprising modified polyvinyl alcohol, and more particularly to a dispersant for emulsion polymerization and suspension polymerization of a vinyl compound, and a dispersant for dispersing a pigment.

[0002]

[Prior Technology and Problems therein]

Polyvinyl alcohol (hereinafter abbreviated as "PVA") is widely employed as a dispersant for emulsion polymerization of a vinyl compound, particularly a vinyl ester represented

by vinyl acetate, and a vinyl ester polymer emulsion obtain by an emulsion polymerization therewith is employed in fields of various adhesives, paints, paper and fiber processing.

[0003]

However, the vinyl ester polymer emulsion is excellent in adhesion property and operation property but is associated with drawbacks of inferior water resistance in a film and a large temperature dependence in the emulsion viscosity, and it is known that these properties are dependent significantly on the dispersant employed in the emulsion polymerization.

[0004]

More specifically, the PVA as the dispersant for emulsion polymerization generally includes so-called "completely saponified PVA" with a saponification degree of about 98 mol.% and "partially saponified PVA" with a saponification degree of about 88 mol.%, and the use of the former provides a relatively good water resistance but results in a drawback that the emulsion viscosity shows a significant increase at a low temperature, thus easily causing a gelation. On the other hand, the use of the latter improves the viscosity increase of the emulsion at the low temperature and the gelling tendency, but results in a drawback that the film has an inferior water resistance.

[0005]

In order to alleviate such drawbacks, the combined use

of both PVAs or the use of PVA of an intermediate saponification degree of the both is tried, but cannot sufficiently satisfy the water resistance of the film and the low temperature dependence of the emulsion viscosity. Also for improving the water resistance of the film, it is also conducted to add an urea resin or various crosslinking agents to a polymer emulsion obtained with a partially saponified PVA as the dispersant. These methods improve the water resistance to a certain extent, but deteriorate the working property at the use for example by a viscosity increase, and cannot provide a sufficiently satisfactory result.

[0006]

Also in suspension polymerization of a vinyl compound such as vinyl chloride or the like, partially saponified PVA or a cellulose derivative such as methyl cellulose or carboxymethyl cellulose has been employed as a dispersant.

[0007]

In suspension polymerization of a vinyl compound, a dispersant is an important factor governing the quality of an obtained polymer, and, performances generally required for the dispersant include (i) an ability to show a high dispersing power with a small amount of use and to provide a particle size distribution as sharp as possible in the obtained polymer particles, (ii) an ability to form the polymer particles as uniform as possible and to form porous particles, in order to

increase an absorbing speed for a plasticizer thereby facilitating the working property, to facilitate removal of a vinyl monomer remaining in the polymer particles, and to prevent formation of a fish eye in a molded product, and (iii) an ability of forming polymer particles of a high packed bulk density.

[0008]

However the aforementioned dispersants for suspension polymerization employed conventionally do not satisfy these requirements but are associated with drawbacks of having a low ability of forming porous polymer particles, being incapable of increasing the plasticizer absorbing speed of the polymer and a difficulty in the removal of the remaining vinyl monomer. Also the dispersant is generally required to have a high dispersing power and to generate a dispersion liquid of a relatively low viscosity and a high concentration.

[0009]

[Problems to be Solved by Invention]

An object of the present invention is to provide a dispersant capable of resolving the drawbacks of the prior PVA dispersant for emulsion polymerization and suspension polymerization, and capable, when employed in an emulsion polymerization of a vinyl compound, of providing a polymer emulsion showing an excellent water resistance in a generated film and a low temperature dependence of viscosity, and, when

employed in a suspension polymerization of a vinyl compound, of generating a polymer constituted of uniform porous particles showing a high plasticizer absorbing speed and enabling an easy removal of a remaining monomer.

[0010]

Another object of the present invention is to provide a dispersant showing a high dispersing power to a dispersed substance such as a pigment or the like, and capable of generating a dispersion liquid of a relatively low viscosity and a high concentration.

[0011]

[Means for Solving Problems]

The aforementioned objects can be attained by a dispersant comprising modified polyvinyl alcohol containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol. %.

[0012]

The modified PVA containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol. % employed in the present invention can be obtained by saponifying a copolymer of a vinyl ester and α -olefin with 4 carbon atoms or less. The vinyl ester can be, for example, vinyl formate, vinyl acetate, or vinyl propionate, but vinyl acetate is preferable economically.

[0013]

α -olefin to be copolymerized with the vinyl ester has 4 carbon atoms or less, and can be, for example, ethylene,

increase an absorbing speed for a plasticizer thereby facilitating the working property, to facilitate removal of a vinyl monomer remaining in the polymer particles, and to prevent formation of a fish eye in a molded product, and (iii) an ability of forming polymer particles of a high packed bulk density.

[0008]

However the aforementioned dispensants for suspension polymerization employed conventionally do not satisfy these requirements but are associated with drawbacks of having a low ability of forming porous polymer particles, being incapable of increasing the plasticizer absorbing speed of the polymer and a difficulty in the removal of the remaining vinyl monomer. Also the dispersant is generally required to have a high dispersing power and to generate a dispersion liquid of a relatively low viscosity and a high concentration.

[0009]

[Problems to be Solved by Invention]

An object of the present invention is to provide a dispersant capable of resolving the drawbacks of the prior PVA dispersant for emulsion polymerization and suspension polymerization, and capable, when employed in an emulsion polymerization of a vinyl compound, of providing a polymer emulsion showing an excellent water resistance in a generated film and a low temperature dependence of viscosity, and, when

employed in a suspension polymerization of a vinyl compound, of generating a polymer constituted of uniform porous particles showing a high plasticizer absorbing speed and enabling an easy removal of a remaining monomer.

[0010]

Another object of the present invention is to provide a dispersant showing a high dispersing power to a dispersed substance such as a pigment or the like, and capable of generating a dispersion liquid of a relatively low viscosity and a high concentration.

[0011]

[Means for Solving Problems]

The aforementioned objects can be attained by a dispersant comprising modified polyvinyl alcohol containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol. %.

[0012]

The modified PVA containing an α -olefin unit with 4 carbon atoms or less by 1 - 10 mol. % employed in the present invention can be obtained by saponifying a copolymer of a vinyl ester and α -olefin with 4 carbon atoms or less. The vinyl ester can be, for example, vinyl formate, vinyl acetate, or vinyl propionate, but vinyl acetate is preferable economically.

[0013]

α -olefin to be copolymerized with the vinyl ester has 4 carbon atoms or less, and can be, for example, ethylene,

propylene, n-butene, or isobutylene, but ethylene is preferable in consideration of the water resistance of the obtained polymer film. A content of α -olefin in the modified PVA is 1 - 10 mol.%, preferably 2 - 8 mol.%. A content of α -olefin less than 1 mol.% cannot provide the aforementioned evident effects, and a content exceeding 10 mol.% lowers a solubility in water, thus being unable to provide the aforementioned effects.

[0014]

In the modified PVA of the invention, another function group for example a carboxyl group, a lactone group, an amide group or an amino group may be introduced within an extent not interfering with the scope of the invention. The modified PVA of the invention preferably has a saponification degree within a range of 50 - 99 mol.%. Also a polymerization degree is selected suitably within a range of 100 - 8,000.

[0015]

Representative applications of the modified PVA of the invention are a dispersant for emulsion polymerization and suspension polymerization of a vinyl compound. Representative examples of the emulsion polymerization and suspension polymerization of vinyl compound include an emulsion homopolymerization of a vinyl ester represented by vinyl acetate, and an emulsion copolymerization of vinyl acetate and ethylene, propylene, vinyl chloride, an acrylate

ester or a methacrylate ester; and a suspension polymerization of vinyl chloride, styrene, methyl methacrylate and other methacrylate esters.

[0016]

The modified PVA of the invention, when employed as a dispersant for an emulsion polymerization, is employed by 0.1 - 20 wt.%, preferably 0.3 - 15 wt.% with respect to the vinyl compound. An amount of use less than 0.1 wt.% results in a poor stability of polymerization, and an amount exceeding 20 wt.% reduces the water resistance of the obtained emulsion. The modified PVA dispersion for emulsion polymerization of the invention is preferably used singly, but another protective colloid or an emulsifier may be used within an extent not affecting the object of the present invention. For example conventional PVA, starch, polyacrylamide, hydroxyethyl cellulose, a known nonionic or anionic emulsifier etc. may be used in combination.

[0017]

The modified PVA dispersant of the invention, when employed as a dispersant for a suspension polymerization, can be used in the same manner as the prior PVA dispersant. Also the modified PVA dispersant of the invention, showing a high dispersing power to various dispersed substances including inorganic and organic pigments, can be utilized in place for prior dispersants in various field. In particular, when

employed as a dispersant for a pigment, it provides a dispersion liquid of a lower viscosity and an improved dispersion stability in comparison with various prior dispersants.

[0018]

[Effect of the Invention]

The modified PVA dispersant of the invention, when employed as a dispersant for an emulsion polymerization of a vinyl compound, can provide a polymer emulsion with an excellent water resistance in the generated film and a low temperature dependence of the viscosity. Also when employed as a dispersant for a suspension polymerization, it can provide suspension polymer particles which show a sharp particle size distribution, are porous and have a high packed bulk density. Such suspension polymer has characteristics of a high absorption speed of a plasticizer, an easy removal of the remaining monomer, a low powder scattering at the handling, and a satisfactory fitting into a molding machine.

[0019]

Also the modified PVA dispersant of the invention shows a high dispersing power for a dispersed substance. In particular, when employed as a dispersant of a pigment, it can form a dispersion liquid of a lower viscosity and an improved dispersion stability, in comparison with many prior dispersants.

[0020]

[Examples]

In the following, the modified PVA dispersant of the invention will be explained more specifically by examples. In the examples, "part" is based on weight.

Example 1

(Production of modified PVA) 100 parts of vinyl acetate and 30 parts of methanol were charged in a reactor equipped with an agitator, and, after nitrogen substitution, 3 parts of ethylene were added. Then, as an initiator, a solution was prepared by dissolving 2,2'-azobisisobutyronitrile in methanol, and was subjected to a nitrogen substitution by bubbling with nitrogen gas. The reactor containing the aforementioned monomers was heated, and the initiator solution was added when the internal temperature reached 60°C to initiate polymerization. It was cooled when a polymerization rate reached 48% after 3 hours. After elimination of ethylene, the unreacted vinyl acetate monomer was eliminated under a reduced pressure to prepared a methanol solution, which was saponified by an addition of an NaOH methanol solution. The obtained modified PVA showed a polymerization degree of 1,200, a saponification degree of 90.0 mol.%, and an ethylene content of 7.2 mol.%.

[0021]

(Emulsion polymerization of vinyl acetate) In a reactor equipped with an agitator, a reflux condenser, a thermometer,

and a dropping funnel, 20 of the aforementioned PVA were dissolved in 240 g of water. Then 20 g of vinyl acetate were added, and 0.3 g of hydrogen peroxide and 0.5 g of tartaric acid were added when the internal temperature reached 70°C to initiate polymerization. Then 180 g of vinyl acetate and 0.3 g of hydrogen peroxide were added continuously over 3 hours. After the addition was completed, the internal temperature was maintained at 80°C for 1 hours for executing ripening. After cooling, 20 g of dibutyl phthalate were added to obtain an emulsion with a non-volatile portion of 48.0 % and a viscosity of 12,000 cp at 30°C.

[0022]

The obtained emulsion was subjected to following tests:

(1) Evaluation of temperature dependence of emulsion viscosity:

An emulsion viscosity was measured at 30°C and 0°C, and the temperature dependence was evaluated by a viscosity ratio (0°C/30°C).

(2) Stability in low-temperature standing:

The emulsion was let to stand for 24 hr. at -5°C and a change in the emulsion was observed.

(3) Water resistance:

A paper/paper adhesion test was executed under following conditions, then a peeling was executed after a drying by standing for 1 day and after an immersion for 24 hours in water

of 30°C, and the adhesion state was evaluated in three levels (A: very good, B: good, and C: poor):

paper: B-liner, 25 x 50 mm, 5 pieces each

coating amount: 40 g (wet)/m²

pressurizing: pressurized once with a hand roller

standing: 23°C, 65%RH, 24 hr

Results are shown in Table 1.

[0023]

Examples 2, 3

(Production of modified PVA) Two modified PVAs were prepared by the same operations as in Example 1 except for a change in the monomer composition.

(Emulsion polymerization of vinyl acetate) An emulsion polymerization of vinyl acetate was conducted by the same operation as in Example 1, utilizing each of the aforementioned PVAs as the dispersant, and the obtained emulsion was evaluated. Results are shown in Table 1.

[0024]

Comparative Examples 1 and 2

(Production of PVA) Unmodified PVAs were prepared by the same operations as in Example 1 except for a change in the monomer composition.

(Emulsion polymerization of vinyl acetate) An emulsion polymerization of vinyl acetate was conducted utilizing each of the aforementioned PVAs as the dispersant, and the obtained

emulsion was evaluated. Results are shown in Table 1.

[0025]

[Table 1]

Polymerization formulation for vinyl acetate and characteristics of polymer emulsion

Example	PVA dispersant				Polymer emulsion characteristics				
	saponification degree *1 (mol.%)	ethylene content (mol.%)	polymerization degree	solid content (wt.%)	viscosity immediately after formation (mPas·S)	viscosity at 0°C (mPas·S)	viscosity ratio 0°C/30°C	state at -5°C (after standing for 24hr)	water resistance
Example 1	90.0	7.2	1,200	48.0	12,000	30,000	2.5	flowable	A
Example 2	85.0	10.0	500	47.9	9,000	24,300	2.7	flowable	A
Example 3	94.0	4.0	1,700	47.8	28,000	72,800	2.6	flowable	A
Comparative Example 1	98.0	0	1,700	48.1	15,800	192,800	12.2	gelled	B
Comparative Example 2	88.0	0	1,700	48.4	41,000	114,800	2.8	flowable	C

*1 vinyl alcohol content

From the results shown in Table 1, it is evident that the modified PVA dispersant of the invention can form a film of a satisfactory water resistance and can provide an emulsion with a low temperature dependence of the emulsion viscosity.

[0026]

Examples 4 - 6 and Comparative Example 3

(Suspension polymerization of vinyl chloride)

A modified PVA and an unmodified PVA were prepared by executing operations similar to those of Example 1 except for a change in the monomer composition. Suspension polymerization of vinyl chloride was executed, employing these, singly or with another PVA, as a dispersant.

[0027]

In a glass-lined autoclave, 40 parts of deionized water, 0.75 parts of a 2 wt.% aqueous solution of a PVA dispersant and 0.009 parts of a 50 wt.% toluene solution of diisopropyl peroxydicarbonate were charged, and, after the interior of the autoclave was evacuated to 50 mmHg to eliminate oxygen, 30 parts of a vinyl chloride monomer were charged and subjected to a polymerization by heating to 57°C under agitation. The pressure in the autoclave was 8.5 kg/cm² at the start of the polymerization but reached 4.5 kg/cm² after 7 hours from the start of polymerization. The polymerization was terminated at this point, and the unreacted vinyl chloride monomer was purged, and a content was taken out and dried by dehydration.

Physical properties and an amount of use of the PVA dispersants are shown in Table 2, and characteristics of the obtained vinyl chloride resin are shown in Table 3. The vinyl chloride resin showed a polymerization yield of 85 % and an average degree of polymerization of 1050.

[0028]

Characteristics of the obtained vinyl chloride resin were evaluated by following criteria:

- (1) Particle size distribution: Measured by a dry sieve analysis utilizing Tyler mesh based metal sieves.
- (2) Packed bulk density : Measured according to JIS K6721-1959.
- (3) Uniformity of porosity of particles: A mixture of 100 parts of the vinyl chloride resin, 50 parts of dioctyl phthalate, 1 part of dibutyl tin maleate, 1 part of cetyl alcohol, 0.25 parts of titanium white, and 0.1 parts of carbon black was kneaded with rolls of 150°C for a predetermined time (3, 5 or 7 minutes) to prepare a sheet of a thickness of 0.2 mm, and a number of fish eyes per 100 cm² of the sheet was counted in a transmitting light. Elimination of fish eyes within a shorter time indicates a better uniformity of porosity of the particles.

[0030]

- (4) Plasticizer absorbing property: In a planetary mixer connected to a plastograph, 100 parts of the vinyl chloride

resin and 50 parts of dioctyl phthalate were charged into a container kept at 80°C, then a kneading torque was measured at different times during agitation, and there was indicated a kneading time when the kneading torque was lowered. A shorter time indicates a better absorbing property for the plasticizer.

(5) Residual vinyl chloride monomer: A predetermined amount of the vinyl chloride resin was dissolved in tetrahydrofuran, and a vinyl chloride monomer content in the vinyl chloride resin was determined by a gas chromatograph.

[0031]

[Table 2]

Polymerization formulation of vinyl chloride

Example	PVA dispersant				co-used PVA dispersant		
	saponification degree *1 (mol.%)	polymerization degree	ethylene content (mol.%)	used amount *2 (wt%/VCM)	saponification degree *1 (mol.%)	polymerization degree	used amount *2 (wt%/VCM)
Example 4	75	700	5.0	0.06	-	-	-
Example 5	80	1,800	10.0	0.06	-	-	-
Example 6	30	200	8.0	0.04	80	200	0.04
Comparative Example 3	80	2,000	0	0.06	-	-	-

*1 vinyl alcohol content

*2 wt.% to vinyl chloride monomer (VCM).

[0032]

[Table 3]

Characteristics of vinyl chloride resin

Example	Particle size distribution (wt. %)			Bulk density (g/cc)	Uniformity of particle porosity (number of fish eyes)			Plasticizer absorption (min)	Residual vinyl chloride monomer (ppm)
	42 mesh pass	100 mesh pass	250 mesh pass		3 min	5 min	7 min		
Example 4	100	56	0	0.551	40	1	0	5.3	0.7
Example 5	100	50	0	0.550	39	2	0	5.1	0.6
Example 6	100	53	0	0.530	35	0	0	4.2	0.1
Comparative Example 3	100	38	0	0.492	700	50	13	15.0	120

The results of Table 3 indicate that a suspension polymerization utilizing the modified PVA dispersant of the invention either singly or in combination of an already known PVA provides a vinyl polymer constituted of uniform porous particles, showing a high plasticizer absorbing speed and allowing easy removal of the residual monomer.

[0033]

Examples 6, 7 and Comparative Examples 4, 5

(Preparation of calcium carbonate) Modified PVA and unmodified PVA were prepared in a method similar to that in the foregoing examples, and were used as a dispersant for preparing a paste of calcium carbonate (P-3 manufactured by Shiraishi Kogyo Co.) of a concentration of 60 wt/%. The paste was let to stand for 3 months at 20°C, and a dispersion state was evaluated in three levels (A: no change in dispersion state, B: slight sedimentation, C: considerable sedimentation). For

the purpose of comparison, a paste was prepared by employing sodium polyacrylate as a dispersant and was evaluated in a similar manner. Results are shown in Table 4.

[0034]

[Table 4]

Example	PVA dispersant				Calcium carbonate dispersion	
	saponification degree *1 (mol.%)	polymerization degree	ethylene content (mol.%)	used amount (wt%/calcium carbonate)	viscosity (30°C) (mPa·s)	stability after standing
Example 6	85	200	5.0	1.0	150	A
Example 7	88	300	10.0	1.0	200	A
Comparative Example 4	38	300	0	1.0	1,500	C
Comparative Example 5	sodium polyacrylate			1.0	850	B

*1 vinyl alcohol content

Results in Table 4 indicate that modified PVA dispersant of the present invention can provide a dispersion with a low viscosity and a satisfactory dispersion stability.

IN RE: OPPOSITION TO EP-B-1420033

D1E

Section 1 - Experimental Details

Examples 1 to 3 of Japanese patent application JP-A-6-80709 were repeated.

Viscosity and Tg values were measured.

Section 2 – Measurement of Viscosities

Höppler viscosities (20°C, DIN53015) of 4% solutions of ethylene modified PVAs were measured. Results of the measurements are shown below in Table 1A.

Table 1A

	Ethylene Modified PVA			Höppler Viscosity (mPas) of 4% Solution of Ethylene Modified PVA
	Saponification (mol%)	Ethylene Content (mol%)	Polymerization	
Ex. 1	90.0	7.2	1200	12.5
Ex. 2	85.0	10.0	500	5.5
Ex. 3	94.0	4.0	1700	26.0

Section 3 – Measurement of Tg Values

Tg of polymers (polyvinyl acetate) were measured (DSC method). Results of the measurements are shown below in Table 1B.

Table 1B

	Ethylene Modified PVA			Tg (°C)
	Saponification (mol%)	Ethylene Content (mol%)	Polymerization	
Ex. 1	90.0	7.2	1200	30
Ex. 2	85.0	10.0	500	30
Ex. 3	94.0	4.0	1700	30